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**EFFECT OF SURFACTANT MOLECULAR WEIGHT ON  
PARTICLE MORPHOLOGY OF  $\text{SmCo}_5$   
PREPARED BY HIGH ENERGY BALL MILLING  
(POSTPRINT)**

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<b>14. ABSTRACT</b>  Surfactant-assisted high energy ball milling (HEBM) is a widely used technique for producing nanostructured magnetic materials with oleic acid (OA) being the most commonly utilized surfactant reported in literature to date. No conclusive explanation has been presented for the wide use of OA and only a few studies have deviated from its use. OA has a boiling point of 360 °C which presents issues for complete removal of the surfactant after the HEBM process. Exposing the nanostructured materials to the high temperatures required for surfactant removal is known to result in grain growth and oxidation. In other studies, select surfactant systems, such as octanoic acid or oleylamine, have been used, however, a systematic study examining the dependence of surfactant selection on overall particle (flake) morphology has yet to be performed. In this study, we have qualitatively and quantitatively examined the effects of surfactant selection on the morphology and magnetic properties of SmCo <sub>5</sub> utilizing surfactants with lower boiling points that are structurally similar to OA. Our results demonstrate that there was little change in the morphological and magnetic properties for the different surfactants. The implication is that lower boiling point surfactants may be used for HEBM, which require less severe conditions for surfactant removal after milling thereby preserving the integrity of the powders.					
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# Effect of surfactant molecular weight on particle morphology of $\text{SmCo}_5$ prepared by high energy ball milling

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Surfactant-assisted high energy ball milling (HEBM) is a widely used technique for producing nanostructured magnetic materials with oleic acid (OA) being the most commonly utilized surfactant reported in literature to date. No conclusive explanation has been presented for the wide use of OA and only a few studies have deviated from its use. OA has a boiling point of 360 °C which presents issues for complete removal of the surfactant after the HEBM process. Exposing the nanostructured materials to the high temperatures required for surfactant removal is known to result in grain growth and oxidation. In other studies, select surfactant systems, such as octanoic acid or oleylamine, have been used, however, a systematic study examining the dependence of surfactant selection on overall particle (flake) morphology has yet to be performed. In this study, we have qualitatively and quantitatively examined the effects of surfactant selection on the morphology and magnetic properties of  $\text{SmCo}_5$  utilizing surfactants with lower boiling points that are structurally similar to OA. Our results demonstrate that there was little change in the morphological and magnetic properties for the different surfactants. The implication is that lower boiling point surfactants may be used for HEBM, which require less severe conditions for surfactant removal after milling thereby preserving the integrity of the powders. © 2012 American Institute of Physics. [doi:10.1063/1.3677760]

## I. INTRODUCTION

Surfactant-assisted high energy ball milling (HEBM) has emerged as a valuable technique for producing micron or nano-scale powders with nano-scale features for numerous applications throughout the materials community. Manipulation of the initial powder charge, surfactant concentration, temperature, milling media, and milling time provides a high level of control over the product morphology, particle size, grain-size, interfacial surface area, and specific surface area.<sup>1</sup> HEBM has been employed within the magnetic materials community as a method for producing rare-earth magnetic nanoparticles and nanostructured powders.<sup>2</sup> Surfactants play a critical role in the HEBM process as these molecules typically contain a functional moiety that can physically, chemically or electrostatically interact with the metal or material as it undergoes deformation and new surfaces are exposed. The surfactant molecules bind to these new surfaces resulting in the formation of a thin organic layer that protects the exposed surface from cold welding when it comes into contact with another surface later in the milling process. The powder/surfactant ratio can be varied to induce a variety of structures, morphologies, and features into the final product. Recently, surfactant assisted HEBM has been used in the production of a variety of nanostructured  $\text{SmCo}_5$  powders

with morphologies ranging from flakes to spherical particles with diameters less than 30 nm.<sup>3–7</sup>

Although essential to the HEBM process, surfactants often need to be removed after milling and prior to consolidation or else the temperatures and/or pressures required for consolidation can lead to decomposition of the surfactant and/or reaction with the metal yielding impurities in the final product. Surfactant removal is most often achieved through a vacuum annealing process which requires the use of relatively high temperatures and long dwell times. Subjecting the nanostructured powders to the high temperatures required for surfactant removal is known to result in grain growth and oxidation.<sup>7,8</sup> Oleic acid (OA) is the most commonly utilized surfactant reported in literature for the preparation of  $\text{SmCo}_5$  nanoflakes.<sup>5–7,9</sup> Interaction of OA acid with  $\text{SmCo}_5$  occurs through the formation of a carboxylate bond between the carboxylic acid head of the surfactant and the metallic  $\text{SmCo}_5$  surface (inset Fig. 1). Temperatures of 500 °C or higher are required for removal of OA (bp = 360 °C) bound to a  $\text{SmCo}_5$  surface, under atmospheric conditions, due to this chemical interaction. In order to preserve the nanoscale features obtained during the HEBM process it would be desirable to employ a surfactant system that does not require such severe temperatures or long annealing times for removal. Herein we report a systematic investigation into the use of several saturated fatty acid surfactants for the HEBM of  $\text{SmCo}_5$  to yield flakes. By lowering the molecular weight (MW) of the surfactant, and subsequently reducing its boiling point (Fig. 1), we

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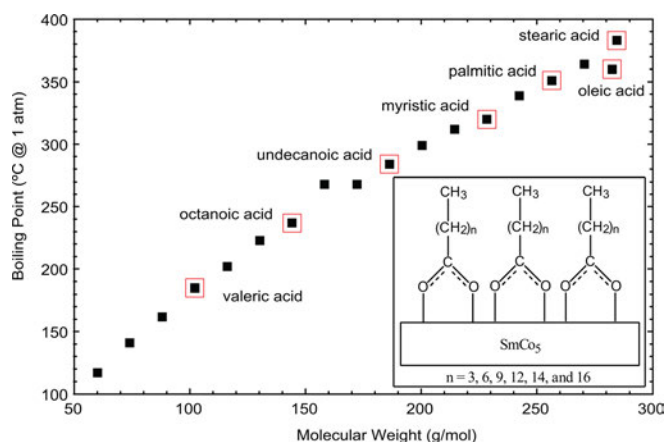


FIG. 1. (Color online) Boiling point with respect to surfactant molecular weight for the free (unbound) molecule. Inset: Illustration of the carboxylate bonding of a fatty acid to  $\text{SmCo}_5$  surface resulting in the formation of an organic film.

demonstrate that surfactant removal at lower temperatures is possible for low MW fatty acid surfactants with minimal changes to the powder morphology or magnetic properties.

## II. EXPERIMENTS

Samples were prepared from a  $\text{SmCo}_5$  as-cast alloy with a particle size of 1-5 mm and a columnar grain size of 50-800  $\mu\text{m}$ . Heptane was purchased from Acros Organics and was used as the solvent at a concentration equivalent to 55% by weight of the powder. Oleic acid (Fisher Scientific), myristic acid (Aldrich), octanoic acid (Acros Organics), stearic acid (Aldrich), palmitic acid (Aldrich), undecanoic acid (Aldrich), and valeric acid (Aldrich) were used as received at a concentration equivalent to 30% by weight of the powder. Details of the procedure for preparing  $\text{SmCo}_5$  flakes with OA as the surfactant are as follows. A steel vial containing 10 g of 3/32 in. diameter 52-100 steel milling balls was charged with  $\text{SmCo}_5$  powder (5.0 g) and combined with heptane (2.75 g), OA (1.5 g) and sealed under an argon atmosphere to prevent oxidation. The vial was loaded into a SPEX 8000 D mill for 1 h. After milling, each powder sample was washed with acetone and dried under vacuum. The powders were characterized using scanning electron microscopy (SEM, FEI Quanta ESEM), X-ray diffraction (Rigaku DMAX B RU200 XRD), and differential scanning calorimetry (DSC, PerkinElmer DSC 8000). The DSC tests were completed with a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under a 20 ml/min flowing ultrahigh purity argon atmosphere. Each sample was heated to 600  $^{\circ}\text{C}$  and held isothermally for 5 min, ballistically cooled to 30  $^{\circ}\text{C}$ , and reheated to 600  $^{\circ}\text{C}$ . The second heating curve was used for subtraction (assuming full expulsion of surfactants at 600  $^{\circ}\text{C}$ ). X-ray diffraction (XRD) was done using Cu K $\alpha$  radiation to confirm the 1:5 phase and estimate the grain size of each sample. To determine the coercivity, a closed loop magnetic hysteresis graph (KJS MG-700) was employed. For these measurements the powders were mixed with a two-part epoxy in polyurethane molds, magnetically aligned using a pulse magnetizer with a field of 10 T (each sample pulsed 3X), then cured for 12 h at room temperature in a 1 T field.

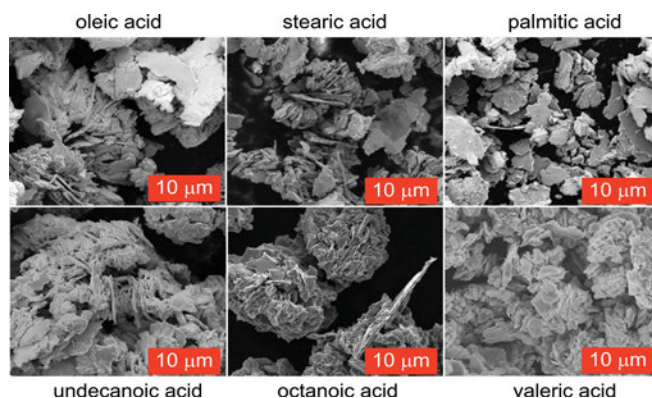


FIG. 2. (Color online) SEM images of  $\text{SmCo}_5$  powders made with different surfactants.

## III. RESULTS AND DISCUSSION

### A. Powder morphology

The fatty acids used in this study were selected with regard to their chemical and structural similarity to OA, each containing a carboxylic acid head group and a hydrocarbon tail. The length of the hydrocarbon tail was systematically reduced to provide a lower MW and boiling point. As shown in Fig. 2, all of the surfactants used in this study produced the desired flake morphology, however, there does appear to be a minor correlation between the average flake size and the surfactant MW with fewer large flakes present in the powders produced using low MW surfactants. Throughout the open literature surfactant concentrations are commonly reported as a percentage (wt%) with respect to the powder mass. This can be misleading if there is a significant difference in the MW of the surfactants under investigation. For example, for a fixed concentration of 30 wt% valeric acid yields nearly three times the number of surfactant molecules (14.2 mmol) as OA (5.3 mmol) for a powder charge of 5 g. Although no observable change in the average grain size was observed from XRD measurements (Fig. 3), SEM analysis of the respective powders demonstrates that smaller flake sizes and thicknesses are obtained for valeric acid and octanoic acid in comparison to OA or the other higher MW surfactants. The particle lengths ranged from 0.5 to 10  $\mu\text{m}$ , where the OA sample was on the higher end of this range and the valeric acid sample was on the lower end. The range of the trend toward decreasing flake size and thickness with low

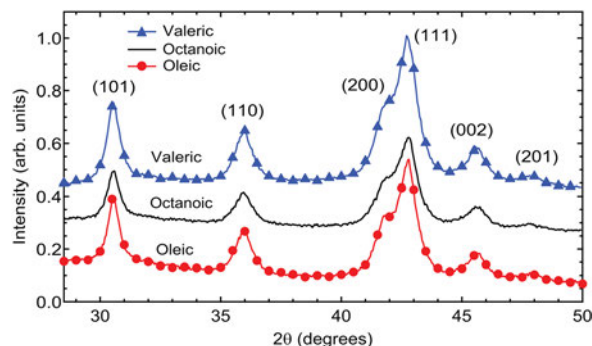


FIG. 3. (Color online) X ray diffraction patterns for  $\text{SmCo}_5$  powders made with different surfactants obtained using Cu K $\alpha$  radiation.

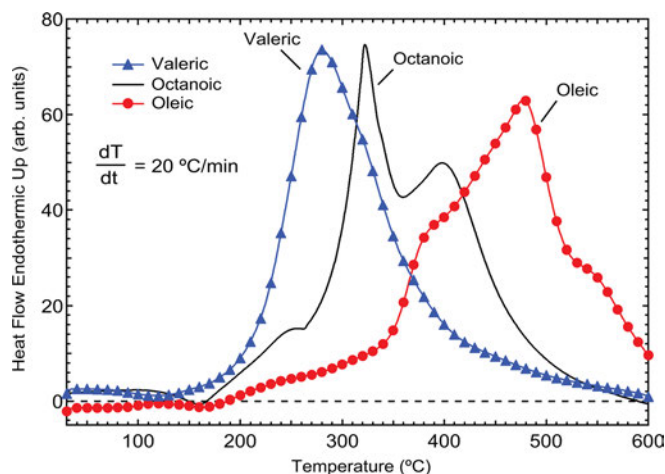


FIG. 4. (Color online) DSC curves for  $\text{SmCo}_5$  prepared with different surfactants. Measurements taken at a heating rate of  $20^\circ\text{C}/\text{min}$  in Ar atmosphere.

MW surfactants is likely attributed to the increased number of molecules available which are able to bind to the new surfaces formed during the milling process resulting in a product with an overall higher specific surface area.

## B. Surfactant removal

The acting hypothesis for this investigation was that lower MW surfactants, if capable of yielding a similar powder morphology, possess significantly lower boiling points and therefore should require shorter annealing times and lower temperatures to remove the surfactant after the milling process. In general, as the hydrocarbon tail of a fatty acid is decreased in length by four carbons an approximately  $100^\circ\text{C}$  decrease in the boiling point is observed. To test this theory we performed a series of differential scanning calorimetry (DSC) experiments on all of the milled powders to observe variations in heat flow with respect to the temperatures required for surfactant dissociation/desorption and evaporation from the metal surface. The DSC data presented in Fig. 4 suggests that dissociation/desorption and evaporation occur at significantly lower temperatures for valeric acid and octanoic acid when compared to the temperatures required for removal of OA and the other high MW surfactants.

To determine the average temperature of surfactant removal the first moment of the curves presented in Fig. 4,  $\langle T \rangle$ , was calculated by integration over the heat flow,  $\mathcal{F}$ ,

$$\langle T \rangle = \frac{\int T \mathcal{F} dT}{\int \mathcal{F} dT}. \quad (1)$$

The results, given in Table I, clearly show that the average temperature of surfactant removal is higher than the surfactant boiling point with a roughly linear relationship of  $\langle T \rangle = 0.63 \times T_{\text{BP}} + 201^\circ\text{C}$ . It is worthy to note that these temperatures are higher than the boiling points for those respective surfactants due to the chemical interaction of the surfactant with the metal surface. Additionally, the shape of the DSC curves and area under them strongly depend on heating rate. As all measurements have been performed with the same heating rate the curves in Fig. 4 are useful for comparative purposes.

TABLE I. Measured properties of  $\text{SmCo}_5$  flakes produced by high energy ball milling.

Surfactant	Grain size nm	$\langle T \rangle$ $^\circ\text{C}$	Coercivity kOe
Stearic Acid	$29 \pm 3$	420	16.2
Oleic Acid	$24 \pm 4$	456	15.3
Palmitic Acid	$23 \pm 3$	418	16.6
Myristic Acid	$21 \pm 3$	398	15.7
Undecanoic Acid	$24 \pm 5$	376	16.6
Octanoic Acid	$23 \pm 4$	356	19.0
Valeric Acid	$22 \pm 2$	312	20.1

## C. Magnetic properties

The magnetic coercivity results of the closed loop hysteresis graph measurements are presented in Table I. As a function of the surfactant MW, there was little change in the coercivity for the higher MW surfactants. However, the samples prepared with octanoic and valeric acid showed a markedly higher coercivity. Comparison of these results with those presented by Knutson *et al.* suggest that the flake thickness is reduced with the lower MW surfactant.<sup>9</sup> A coercivity of 19 kOe is consistent with flake thicknesses of 100-300 nm, whereas coercivities between 15 and 17 kOe correspond to thicknesses of 300-700 nm. These flake thicknesses are also consistent with the SEM measurements performed in this work which further suggests that the presence of additional surfactant in the low MW samples does have some effect on the flake size and thickness.

## IV. CONCLUSIONS

Lowering the MW of the surfactant used in the high energy ball milling process significantly reduces the temperature required to remove the surfactant under a flowing argon atmosphere. This trend is expected to be further enhanced by heating under vacuum. The surfactant MW did not seem to affect the grain size of the powders, however, a minor dependence of the flake size and thickness was observed for the low MW surfactants with those powders displaying fewer large diameter flakes. Coercivity measurements for the  $\text{SmCo}_5$  flakes prepared with the lower MW surfactants vary in accordance with the particle sizes reported by Knutson *et al.*<sup>9</sup>

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